PATENT SPECIFICATION (11) 1 552 151

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(21) Application No. 48398/76 (22) Filed 19 Nov. 1976
(31) Convention Application No. 7 536 891 (19)
(32) Filed 25 Nov. 1975 in
(33) France (FR)
(44) Complete Specification published 12 Sept. 1979
(51) INT CL² C22C 21/06
(52) Index at acceptance
C7A 741 742 743 745 782 783 B249 B25X B25Y B289 B29Y B307 B309 B319 B32Y B335 B337 B339 B349 B357 B359 B35Y B37Y B383 C385 B387 B389 B399 B419 B42Y B433 B435 B437 B439 B459 B46Y B479 B481 B48X B50Y B515 B517 B519 B539 B548 B549 B54Y B558 B559 B55Y B610 B613 B616 B619 B620 B621 B624 B627 B62X B630 B635 B661 B663 B665 B667 B669 B66X B670

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(54) WELDABLE ALUMINIUM ALLOY AND PROCESS FOR THE PRODUCTION OF WELDABLE SHEETS OR PLATES OF SUCH ALLOY

(71) We, CEGEDUR SOCIETE DE TRANSFORMATION DE L'ALUMINIUM PECHINEY, a body corporate organised and existing under the laws of France, of 66 avenue Marceau, 75361 Paris Cedex 08, France, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to an aluminium alloy for use in the production of plates or sheets suitable for welding, a process for the production of self-cooling or quenching metal sheets or plates which are suitable for welding, and to metal sheets or plates produced by the process.

In the manufacture of welded assemblies, it is known to use alloy A—Z5 G (nominal melting range composition by weight <0.2% Si, <0.4% Fe, 0.5 to 1% Cu, 0.05 to 0.3% Mn, 1 to 3% Mg, 0.1 to 0.3% Cr, 3 to 4% Zn, <0.15 % Ti, other ingredients each <0.05% and not more than 0.15% in total, balance, including impurities, aluminium.) This alloy which is suitable for precipitation hardening also has a low critical quenching rate. In the case of products wth a relatively limited thickness, when the hardening elements (in this case MgZn) have been dissolved, cooling in air followed by ageing at ambient temperature is sufficient for progressively hardening the alloy through the formation of Guinier-Preston zones.

This possibility is obviously of considerable interest in the case of members having large dimensions assembled by welding, whereby those portions of the member in the vicinity of the weld bead reach a temperature which is sufficient to re-dissolve the hardening elements. During ageing at ambient temperature the Guinier-Preston zones are reformed which once again brings about the hardening of the alloy.

Unfortunately at a distance from the bead raised to a temperature such that the hardening phases have had the time to coalesce but not to re-dissolve, there is a metal strip which not only does not any longer react to ageing but which in addition has an increased tendency to foliating corrosion.

In addition, an aluminium-magnesium alloy containing about 5% of the latter element is known, whereby said alloy, which does not have a precipitation hardening capacity due to its too low magnesium content, is generally hardened by cold working. However, this treatment, which is carried out without any special precaution, renders the metal very sensitive to intergranular corrosion due to the precipitation along the grain boundaries of a continuous film of β-phase Mg_2Al_3 and Mg_2 Si. To prevent this susceptibility to intergranular corrosion, it is known to carry out so-called desensitisation treatments of the alloy at temperatures between 200 and 250°C and for periods of 8 to 24 hours immediately following cold working. The micrographic structure

obtained then only has discontinuous β-phase islets as opposed to a continuous layer at the grain boundaries.

We have found that by correlating the manganese and chromium contents of an aluminium-manganese-zinc alloy containing nominally by weight from 3.5 to 5% magnesium and from 1.5 to 3% zinc, an identical treatment performed at a slightly higher temperature (200 to 380°C, but preferably 250 to 350°C) of much shorter duration on such an alloy eliminates the tendency to intergranular corrosion such as normally found in Type A—65 alloys of nominal composition by weight 0.05 to 0.2% Mn, 4.3—5.6% Mg, 0.05 to 0.2% G, 0.10% Zn, balance Al, and has also a certain number of surprising effects.

The zone involved by the welding of the thus treated alloy is hardenable by ageing at ambient temperature. Its mechanical characteristics after welding are better than those of A—G5 and close to those of A—Z5 G. They improve over a period of time due to ageing after welding. Finally, in the welded state the alloy has a better stress and foliating corrosion resistance than A—Z5 G.

The invention therefore concerns an alloy of the type Al-Mg-Zn, a production process for weldable sheets or plates made from this alloy and plates for welding produced from this alloy.

According to one aspect of the present invention there is provided an aluminium alloy for use in the manufacture of plates or sheets which after welding have a good resistance to foliating corrosion, comprising the following composition by weight, Si$\leqslant$0.35%, Fe$\geqslant$0.40%, Cu$\leqslant$0.30%, Mn in an amount up to but not exceeding 0.4%, Mg=3.5% to 5%, Cr in an amount up to but not exceeding 0.04%, Zn= 1.5% to 3%, Zr$\leqslant$0.30%, other incidental constituents: in each case $\leqslant$0.05%, Al: the balance excluding impurities and incidental constituents. The process has two main variants, of which the first comprises the following sequence of operations,

1. Homogenisation of the rolling plate, preferably at a temperature in the range of from 400 to 540°C for a time in the range of from 6 to 50 hours.

2. Hot rolling which may, but need not, be performed at homogenisation heat and terminate at a temperature such that the elements which participate in the precipitation hardening remain in solid solution (temperature exceeding 370°C). In the case where hot rolling is not performed at homogenisation heat, i.e. when the plate is cooled after homogenisation, the plate is re-heated to a temperature and for a time such that the elements precipitated on cooling can be restored to solid solution.

3. A sufficiently rapid cooling to ambient temperature to maintain the hardening elements in a supersaturated solid solution, whereby the cooling rate must be greater than the critical quenching rate.

4. Cold rolling to the final thickness.

5. A brief heat treatment at 200—380°C and lasting for a short time of a few minutes, e.g. 6 minutes.

The second variant comprises the following operations:

1. Homogenisation of the rolling plate, preferably at a temperature in the range of from 400 to 540°C for a time in the range of from 6 to 50 hours.

2. Hot rolling which, as in the case of the first variant, can be performed at homogenisation heat, and then warm rolling until the final thickness is obtained with a precise temperature control.

The initial rolling passes excluding the last two are performed at a temperature in excess of that of the usual solution heat treatment temperature for this alloy, i.e. 370°C.

The strip is then cooled, optionally to 380°C, and the two final passes are performed in the temperature range 250 to 380°C.

It is important to note that the initial rolling passes excuding the last two are performed on a reversing mill under industrial conditions resulting in slight cooling, whereas the two final passes are performed on a tandem strip mill, which is a very rapid operation followed by a rapid fall in temperature from 380 to 250°C.

In the initial passes excluding the last two there is therefore a slow temperature drop, e.g. from 520 to 380°C, and then during the two final passes a very rapid temperature drop from 380 to 250°C.

During the different successive operations, the following metallurgical transformations take place relative to the first variant:

1. During homogenisation, the MgZn constituents participitating in the hardening and which may have precipitated on casting are re-dissolved.
2. Hot rolling is subject to two conditions:
Firstly, it must be performed at homogenisation heat so that no precipitation can occur during an intermediate cooling (or in the case where the plate has been cooled after homogenisation, hot rolling must be performed immediately after re-heating such that its duration and temperature make it possible to redissolve the elements which have precipitated during cooling).
Secondly, it must be completed at a temperature such that during the rolling process, no precipitation can occur (temperature above 370°C).
3. Rapid cooling after hot rolling. During this cooling, the hardening elements remain in supersaturated solid solution.
4. Cold rolling. During this operation, dislocations are formed which will subsequently serve as nuclei for the precipitation of the phases.
5. Heat treatment at 200 to 380°C. During this treatment there is a simultaneous precipitation of the β-phase Mg_2Al_3 in the form of discontinuous precipitates and the formation of hardening AlMgZn Guinier-Preston zones.

In the second variant the latter stages of the process are performed on the rolling mill, i.e. after cooling the strip to a temperature between 250 and 380°C, the rolling and heat treatment steps described hereinabove are simultaneously performed on the rolling mill during warm rolling.

In order to obtain the desired mechanical characteristics and corrosion-resistance characteristics, these processes are applied in the manner described hereinbefore to the hereinbefore described alloys of the invention, i.e. whose weight composition falls within the following ranges:

Si $\leqslant$ 0.35%
Fe $\leqslant$ 0.40%
Cu $\leqslant$ 0.30%
Mn in an amount up to but not exceeding 0.4%
Mg 3.5 to 5%
Cr in an amount up to but not exceeding 0.04%
Zn 1.5 to 3%
Zr $\leqslant$ 0.30%
other incidental constituents: each $\leqslant$ 0.05%
Al : the balance excluding impurities and incidental constituents

We have also found that contrary to alloys containing more than 3% of Mg such as 5056 (A—5G), 5083, 5454 or to alloys Al-Zn-Mg such as 7020 (AZ5G) in which manganese and chromium are conventional addition elements, these elements have a disadvantageous influence on foliating corrosion in alloy aluminium based alloys containing 3.5 to 5% Mg and 1.5 to 3% Zn. Thus, and as shown in the following Examples, foliating corrosion which on an alloy treated according to the invention and containing for example 0.40% of manganese and 0.24% of chromium is lower following welding than on a conventional A—Z5G alloy, decreases in a spectacular manner on lowering the chromium content to an amount up to but not exceeding 0.04%, the manganese content remaining equal to or below 0.40%.

Foliating corrosion continues to decrease if the maximum manganese content is lowered to or less than 0.20% and then to or less than 0.05%, whilst maintaining the chromium content at or less than 0.04%. For this latter composition: i.e. Cr$\leqslant$0.04% Mn$\leqslant$0.05%, the sensitivity to foliating corrosion is substantially zero.

The Examples given hereinafter illustrate this phenomenon.

Example 1.

An alloy A outside the invention with the following composition:

Si = 0.15%
Fe = 0.30%
Mn = 0.40%
Mg = 4.52%
Cr = 0.24%
Zn = 2.54%

Zr = 0.10%
Ti = 0.02%
Be = 6 ppm
Al = balance, excluding impurities and incidental constituents,

was cast in plate form by a semi-continuous process. Following homogenisation treatment for 6 hours at 420°C+10 hours at 520°C, the alloy was hot rolled to a thickness of 8 mm at a temperature still above 370°C (temperature at which the elements Mg and Zn in the alloy pass into solution). The thus obtained sheets were quenched in calm air and then cold rolled to a thickness of 4 mm. A heat treatment was then carried out for 6 minutes at 300°C.

The properties obtained were as follows:

$R_{0.2}$ = 26.3 hbar (yield strength)
R_m = 36.7 hbar (ultimate tensile strength)
$A_{5.65}$ = 12.2% (elongation)

These properties are stable with time, i.e. they do not vary over a period of time at ambient temperature.

After MIG welding with filler wire A—G4Z2 the mechanical properties obtained were as given in the following table (weld bead not abraded after welding).

Ageing	7 days	15 days	1 month	2 months	4 months
$R_{0.2}$: hbar	20.9	21.7	22.6	23.0	24.0
R_m : hbar	33.9	34.7	34.8	34.9	35.2
$A_{5.65}$: %	8.2	7.4	6.9	6.7	7.5

These mechanical properties are comparable with those of a conventional A—Z5G alloy (AFNOR Standard A50451), welded under the same conditions as the alloy of the Example as is shown by the following table which indicates the development of mechanical properties of alloy A—Z5G following welding.

Ageing	7 days	15 days	1 month	2 months	4 months
$R_{0.2}$: hbar	15.6	17.5	18.2	19.8	21.2
R_m : hbar	27.9	30.1	31.5	32.5	33.7
$A_{5.65}$: %	7.6	10.4	8.1	9.6	11.0

The mechanical strength level is well above that obtainable with an Aluminum Association of America alloy 5083 (nominal composition by weight 0.3—1% Mn, 4 to 4.9% Mg, 0.03—0.25% Cr, 0.25% Zn, 0.4% Si, 4.4% fe, balance Al) ($R_{0.2}\simeq$13 hbar after welding).

The corrosion resistance of the alloy of Example 1 was determined with reference to an industrial A—Z5G alloy corresponding to AFNOR Standard A 50451.

Foliating corrosion resistance:

The tests were performed at 40°C with permanent immersion in a chromated solution having the following composition:

Sodium chloride	:	3%
Sodium bichromate	:	0.5%
Sodium acetate	:	0.5%
Acetic acid	:	quantity sufficient to give pH 4.

The two unwelded alloys revealed no trace of corrosion after being tested for two months.

This was not the case when they were in the welded state. Following testing for one month, it was found that the two welded alloys had a foliating corrosion zone adjacent to the bead and on either side thereof. The width of the strip which suffered from foliating corrosion was about 3 mm in the case of the alloy of Example 1 and 10 to 12 mm in the case of Alloy A—Z5G. The depth of the corroded part was less in the case of the alloy of Example 1.

As is shown by the following table, this led to a less significant weight loss in the case of the alloy A of Example 1.

Alloy	Weight loss mg/test piece
A	72
A—Z5G	2438

The corrosion kinetics are slower in the case of alloy A. Thus, after testing for two months A—Z5G was completely corroded in the vicinity of the bead (broken test piece), whereas Alloy A still had a thickness of 3 mm (75% of the initial value). The weight loss was on average 10058 mg/test piece.

Stress corrosion resistance:

As in the case of foliating corrosion the sensitivity to stress corrosion A—Z5G varies with the solution temperature but in inverse manner. The higher the solution temperature the more the alloy is susceptible to stress corrosion and the less it is susceptible to foliating corrosion. The selected solution temperature is therefore a compromise between the susceptibility to these two types of corrosion. In addition the stress corrosion resistance and foliating corrosion resistance tests were performed on the same A—Z5G alloy whose solution temperature gives the best compromise. In the unwelded state A—Z5G T6 and Alloy A have no susceptibility to stress corrosion under the following test conditions: stress applied equal to 75% of the yield strength, immersion in chromated solution, life > 60 days.

In the welded state (MIG welding) under 16 hbar load, alloy A did not break after testing for 60 days in a chromate solution, whereas the welded A—Z5G T6 alloy (artificially aged after welding) on average broke after 25 days.

Example 2.

An alloy B outside the invention with the following composition:

Si = 0.15%
Fe = 0.30%
Mn = 0.40%
Mg = 4.52%
Cr = 0.24%
Zn = 2.58%
Zr = 0.10%
Ti = 0.02%
Be = 6 ppm
Al = balance, excluding impurities and incidental constituents,

was cast in the form of plates of industrial dimensions.

After homogenisation treatment for 12 hours at 530°C, the plates were hot rolled to 16 mm and then warm rolled (temperature between 380 and 260°C) until a thickness of 4 mm was reached.

The mechanical properties obtained in the unwelded state are given below:

$R_{0.2}$ = 25.5 hbar
R_m = 35.5 hbar
$A_{5.65}$ = 12%

After TIG welding (ageing after welding) with the filler metal A—G4Z2, they became:

$R_{0.2}$ = 21.7 hbar
R_m = 31.8 hbar
$A_{5.65}$ = 5.3%

Corrosion tests performed under the same conditions as defined in Example 1 showed that the alloy B behaved in exactly the same way as the alloy A of Example 1.

Example 3.

An alloy C outside the invention, of composition:

Si = 0.12%
Fe = 0.30%
Mn = 0.38%
Mg = 4.53%
Cr = 0.12%
Zn = 2.38%
Zr = 0.12%
Ti < 0.02%
Be = 10 ppm
Al = balance, excluding impurities and incidental constituents,

was cast in the form of plates. These plates were then homogenised for 6 hours at 420°C and 6 hours at 540°C. They were then hot rolled at homogenisation heat from 60 to 10 mm, and then after rapid cooling were cold rolled from 10 mm to 5 mm. This was followed by recovery for 5 minutes at 280°C.

The mechanical properties of the welded sheet were as follows:

$R_{0.2}$ = 25.6 hbar
R_m = 36.4 hbar
$A_{5.65}$ = 13.1%

After welding the test pieces by semi-automatic MIG welding with an A—G4Z2 filler wire the following properties were obtained after different ageing periods:

Ageing	7 days	1 month	2 months	4 months
$R_{0.2}$: hbar	20.3	21.1	21.5	21.7
R_m : hbar	31.9	31.9	32.5	32.6
$A_{5.65}$: %	7.6	7.4	7.9	8.1

The results of the foliating corrosion tests performed under the same conditions as in Example 1 revealed a weight loss of 6454 mg/test piece after testing for two months.

Example 4.

An alloy I according to the invention, of composition:

Si = 0.04%
Fe = 0.21%
Mn = 0.37%
Mg = 4.18%
Cr < 0.02%
Zn = 2.46%
Zr < 0.02%
Ti = 0.02%
Be = 50 ppm
Al = balance, excluding impurities and incidental constituents,

was cast in the form of plates. The homogenisation and welding operations were performed as in Example 3.

The mechanical properties of the unwelded sheets were as follows:

$R_{0.2}$ = 25.6 hbar
R_m = 35.7 hbar
$A_{5.65}$ = 14.1%

After welding under conditions identical to those of Example 3 the following properties are obtained:

Ageing	7 days	1 month	2 months	4 months
$R_{0.2}$: hbar	17.4	19.1	20.2	19.7
R_m : hbar	30.0	30.9	32.3	33.7
$A_{5.65}$: %	7.6	8	7.8	9.6

The results of the foliating corrosion tests reveal a weight loss of 4546 mg/test piece after testing for two months.

Example 5.

The same tests as in Examples 3 and 4 were performed on an alloy 2 according to the invention, of composition:

Si = 0.04%
Fe = 0.21%
Mn = 0.19%
Mg = 4.36%
Cr < 0.02%
Zn = 2.48%
Zr < 0.02%
Ti < 0.02%
Be = 20 ppm
Al = balance, excluding impurities and incidental constituents.

The following properties were noted:
Before welding:

$R_{0.2}$ = 24.8 hbar
R_m = 35.0 hbar
$A_{5.65}$ = 14.8%

After welding

Ageing	7 days	1 month	2 months	4 months
$R_{0.2}$: hbar	17.5	19.3	20.6	19.8
R_m : hbar	30.3	31.4	31.5	30.7
$A_{5.65}$: %	8.3	8.1	7.8	6.9

The results of the foliating corrosion tests reveal a weight loss of 1010 mg/test piece after testing for two months.

Example 6.

A plate of alloy 3 according to the invention of the following composition was cast:

Si = 0.04%
Fe = 0.21%
Mn < 0.02%
Mg = 4.58%
Cr < 0.02%
Zn = 2.51%
Zr = 0.25%
Ti < 0.02%
Be = 30 ppm

The rolling and heat treatment process used was the same as that in the previous Examples with the exception that the final recovery was performed for 5 minutes at 230°C.

The following properties were noted:
Before welding:

$R_{0.2}$ = 30.9 hbar
R_m = 39.8 hbar
$A_{5.65}$ = 12.1%

After welding:

Ageing	7 days	1 month	2 months	4 months
$R_{0.2}$: hbar	18.5	20.6	21.8	21.1
R_m : hbar	31.0	34.1	35.3	35.0
$A_{5.65}$: %	7.4	8.2	9.1	7.8

The foliating corrosion tests revealed that there was a weight loss of 322 mg/test piece after testing for two months.

All the results obtained in the above Examples are summarised in the following table as a function of the chromium and manganese composition of the alloy:

Composition	Alloy	Pre-welding characteristics			Post-welding characteristics (after 4 months)			Weight loss after 2 months corrosion
		$R_{0.2}$	R_m	$A_{5.65}$	$R_{0.2}$	R_m	$A_{5.65}$	
Cr = 0.24% Mn = 0.40%	A	26.3	36.7	12.2	24.0	35.2	7.5	10,058
Cr = 0.12% Mn = 0.38%	C	25.6	36.4	13.1	21.7	32.6	8.1	6,454
Cr < 0.02% Mn = 0.37%	1	25.6	35.7	14.1	19.7	33.7	9.6	4,546
Cr < 0.02% Mn = 0.19%	2	24.8	35.0	14.8	19.8	30.7	6.9	1,010
Cr < 0.02% Mn = 0.02%	3	30.9	39.8	12.1	21.1	35.0	7.8	322

The ultimate tensile strength and yield strengths are expressed in hectobars, the elongations as a percentage and he weight losses in mg.

WHAT WE CLAIM IS:—

1. An aluminium alloy for use in the manufacture of plates or sheets which after welding have a good resistance to foliating corrosion, comprising the following composition by weight:

Si $\leqslant$ 0.35%
Fe $\leqslant$ 0.40%
Cu $\leqslant$ 0.30%
Mn in an amount up to but not exceeding 0.4%
Mg=3.5% to 5%
Cr in an amount up to but not exceeding 0.04%
Zn =1.5% to 3%
Zr $\leqslant$ 0.30%
other incidental constituents: in each case $\leqslant$ 0.05%
Al : the balance, excluding impurities and incidental constituents.

2. Aluminium alloy as claimed in claim 1, having the following content limit: Mn $\leqslant$ 0.20%.

3. Aluminium alloy as claimed in claim 1, having the following content limit: $Mn \leqslant 0.05\%$.

4. Process for the production of weldable sheets or plates made from aluminium alloy having improved mechanical properties and corrosion resistance, comprising manufacture of a plate from an aluminium alloy whose composition is in accordance with any one of claims 1 to 3, homogenising said plate at a temperature of 400 to 540°C for 6 to 50 hours, hot rolling the plate at homogenisation heat to an intermediate thickness, said rolling terminating at a temperature above 370°C, followed by rapid cooling to ambient temperature, cold rolling the plate to the final thickness and subjecting it to heat treatment at a temperature of 200 to 380°C for a few minutes.

5. Process for the production of weldable sheets or plates made from aluminium alloy having improved mechanical properties and corrosion resistance, comprising manufacture of a plate from an aluminium alloy whose composition is as claimed in any of claims 1 to 3, homogenising said plate at a temperature of 400 to 540°C for 6 to 50 hours, hot rolling the plate at homogenisation heat to an intermediate thickness, rapidly cooling the plate on the rolling mill to a temperature of 380°C, then warm rolling the plate to the final thickness at a temperature between 250 and 380°C.

6. Process for the production of weldable sheets or plates made from aluminium alloy having improved mechanical properties and corrosion resistance, comprising manufacture of a plate from an aluminium alloy whose composition is as claimed in any one of claims 1 to 3, homogenising said plate at a temperature of 400 to 540°C for 6 to 50 hours, cooling said plate, heating said plate prior to rolling at a temperature and for a time such that the hardening elements which have precipitated during cooling are re-dissolved, followed by hot rolling to an intermediate thickness, said rolling being terminated at a temperature above 370°C, followed by rapid cooling to ambient temperature, cold rolling the plate to the final thickness and subjecting it to heat treatment at a temperature of 200 to 380°C for a few minutes

7. Process for the production of weldable sheets or plates made from aluminium alloy having improved mechanical properties and corrosion resistance, comprising manufacture of a plate from an aluminium alloy whose composition is as claimed in any one of claims 1 to 3, homogenising said plate at a temperature of 400 to 540°C for 6 to 50 hours, cooling said plate, heating said plate prior to rolling at a temperature and for a duration such that the hardening elements which have precipitated on cooling are re-dissolved, followed by hot rolling to an intermediate thickness, rapid cooling on the rolling mill to a temperature of 380°C, followed by warm rolling to a final thickness at a temperature between 250 and 380°C.

8. Process for the production of weldable sheets or plates according to claim 1 substantially as hereinbefore described in Example 4, Example 5, or Example 6.

9. An aluminium alloy according to claim 1, substantially as hereinbefore described.

10. Sheets or plates manufactured according to the process claimed in any one of claims 4 to 8.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1979.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

ELDABLE ALUMINIUM ALLOY AND PROCESS FOR THE PRODUCTION OF WELDABLE SHEETS OR PLATES OF SUCH ALLOY

Patent Number:	GB1552151
Publication date:	1979-09-12
Inventor(s):	
Applicant(s):	CEGEDUR
Requested Patent:	GB1552151
Application Number:	GB19760048398 19761119
Priority Number (s):	FR19750036891 19751125
IPC Classification:	C22C21/06
EC Classification:	C22C21/06; C22F1/047
Equivalents:	BE848630, CH597355, DE2652960, DK524976, FR2333053, IE44313, IE44313L, IT1067583, LU76247, NL7613089

Abstract

Description

(54) WELDABLE ALUMINIUM ALLOY AND PROCESS FOR THE PRODUCTION OF WELDABLE SHEETS OR PLATES OF SUCH ALLOY

(71) We, CEGEDUR SOCIETE DE TRANSFORMATION DE L'ALU MINIUM PECHI-NEY, a body corporate organised and existing under the laws of France, of 66 avenue Marceau, 753611 Paris Cedex 08, France, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:

The invention relates to an aluminium alloy for use in the production of plates or sheets suitable for welding, a process for the production of self-cooling or quenching metal sheets or plates which are suitable for welding, and to metal sheets or plates produced by the process.

In the manufacture of welded assemblies, it is known to use alloy A4Z5 G (nominal melting range composition by weight < 0.2% Si, < 0.4% Fe, 0.5 to 1% Cu, 0.05 to 0.3% Mn, 1 to 3% Mg, 0.1 to 0.3% Cr, 3 to 4% Zn, < 0.15 % Ti, other ingredients each < 0.05% and not more than 0.15% in total, balance, including impurities, aluminium.) This alloy which is suitable for precipitation hardening also has a low critical quenching rate. In the case of products wth a relatively limited thickness, when the hardening elements (in this case MgZn) have been dissolved, cooling in air followed by ageing at ambient temperature is sufficient for progressively hardening the alloy through the formation of Guinier-Preston zones.

This possibility is obviously of considerable interest in the case of members having large